

ADSORPTIVE REMOVAL OF SULFUR COMPOUNDS IN KEROSENE BY USING RICE HUSK ACTIVATED CARBON

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Abstract

Japanese rice husks were carbonized in N₂ at 400°C for 1 h and then were activated in CO₂ at 850°C for 1 h. The capacities of rice husk activated carbons (RHACs) to adsorb refractory sulfur compounds of dibenzothiophenes (DBTs) were evaluated correlating with their textural and chemical characteristics. The RHACs of 0.5 g were soaked in commercial kerosene of 15.0 g at 10°C for 100 h. A micro-porous activated carbon fiber (ACF) having large specific surface area (2336 m²/g) and total pore volume (1.052 cm³/g) was also tested for a comparison purpose. The largest DBTs adsorption capacity (0.069 mg-S/g-Ads and 77 % performance to the ACF) was observed, despite much smaller specific surface area (473 m²/g) and total pore volume (0.267 cm³/g) compared to those of the ACF. Predominant adsorption sites for DBTs in the RHACs were deemed to be slit-shaped micropores of which pore width was less than 0.7 nm.

Introduction

Dibenzothiophenes and its derivatives (hereafter called DBTs) included in fuel oils such as kerosene and diesel oil are refractory poly-aromatic sulfur compounds. In particular, alkyl-substituted DBTs, *i.e.*, 4-methyldibenzothiophene (4-MDBT) and 4, 6- dimethyldibenzothiophene (4, 6-DMDBT), are much refractory (Song and Ma, 2003 and Macaud et al., 2000). Modified hydrodesulfurization under catalysis (Pawelec et al., 2003, Shu et al., 2005 and Zeng et al., 2006) and adsorptive desulfurization using porous materials (Jayne et al., 2005, Ma et al., 2002 and Ng et al., 2005) have been proposed to remove efficiently the refractory DBTs in fuel oils. Selective desulfurization using activated carbons (Ania and Bandosz, 2005 and Zhou et al., 2006), which can be performed at ambient temperature and pressure, has been intensively studied. That is because it seems to be more realistic than the other means on economical basis and operational safety. Toida demonstrated that activated carbon having a specific pore structure attained an efficient and selective removal of DBTs (Toida, 2003). The specific activated carbon is required to have a composite micro-meso porous structure with a large pore volume.

A huge quantity of rice husk (ca. 3 million tons) is produced every year as agricultural waste in Japan. In the present study, rice husk was converted into activated carbon intended for a removal of DBTs from kerosene by employing CO₂ gas activation method. Kerosene is widely used in Japan as a home heating fuel for portable and installed kerosene heaters. Kerosene can be readily purchased at any filling stations or be delivered to homes. Kerosene is a promising fuel oil as hydrogen source of fuel cells for stationary home-use in Japan. The DBTs adsorption capacity of the rice husk activated carbon (RHAC) in commercial kerosene was evaluated, with a correlation with textural and chemical characteristics. A micro-porous activated carbon fiber (ACF) was also tested for a comparison with the RHAC.

Materials and Methods

Material Preparation

Japanese rice husk samples were obtained by rice threshing performed in autumn of 2002, 2003 and 2004. The sample description of the rice husks used is shown in **Table 1**. The raw rice husk of 10 g was carbonized and activated in a stainless steel cylinder (SUS 304) whose respective external and bore diameters were 50 and 44 mm. The rice husk was at first carbonated at 400°C for 1 h in N₂ flow at 500 mL/min. The rice husk was further heated in N₂ flow and finally activated at 850°C for 1 h in CO₂ flow at 500 mL/min. The carbonization and activation process is shown in **Figure 1**. The mass change resulting from the carbonization and activation was measured as mass yield. The commercially available ACF (FR-25, Kuraray Chemical Co., Ltd., Japan) used for the comparison purpose was also given to the similar tests and analysis.

Table 1. Sample description of the Japanese rice husks used in the present study.

Sample ID	Rice brand	Production place	Production year
AK-OH	Akita Komachi	Ohgata, Akita Prefecture	2002
AK-NI	Akita Komachi	Nishiki, Akita Prefecture	2003
AK-OG	Akita Komachi	Ogachi, Akita Prefecture	2003
HI-HO	Hitomebore	Honjo, Akita Prefecture	2003
KO-TO	Koshihikari	Toyooka, Shizuoka Prefecture	2004

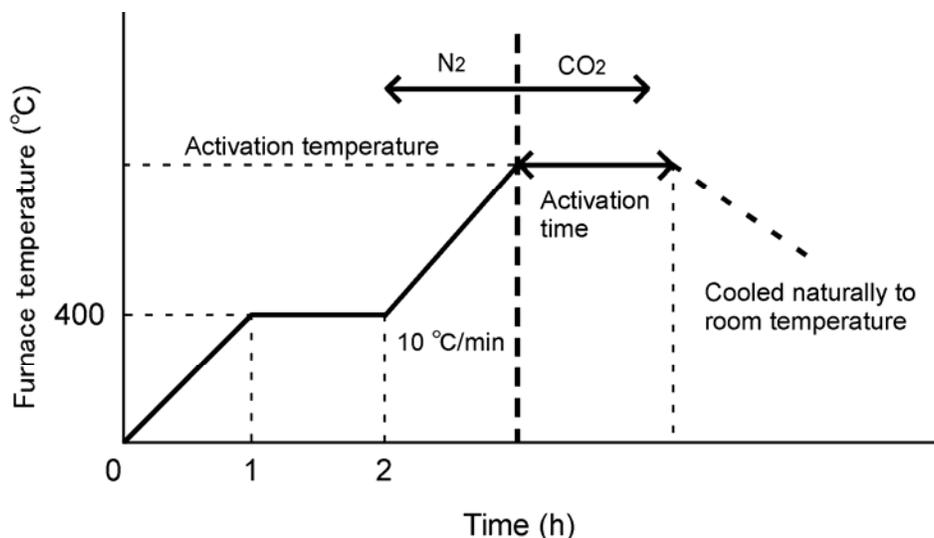


Figure 1. Carbonization and activation process to prepare RHAC.

Compositional Analysis

The ash content of the samples (0.1 g) was precisely determined from the residual-ash ratio after incineration at 800°C for 1 h in air flow (100 mL/min) using a thermogravimetric analyzer (TGA-51; Shimadzu Corp., Japan). A CHN/S analyzer (2400 I; PerkinElmer Inc., USA) was used to determine the hydrogen, carbon, nitrogen and sulfur contents of the samples. All the samples were dried at 105°C for 3 h prior to analyses. The content of oxygen excluding that in ash was determined to be a difference of hydrogen, carbon, nitrogen, sulfur, and ash.

Textural Characterization

Nitrogen adsorption isotherms at -196°C were obtained using a gas adsorption analyzer (Autosorb-3B; Quantachrome Instruments Inc., USA). The sample of 0.05 g was degassed at 200°C for > 3 h prior to the isotherm measurement. The BET specific surface area (S_{BET}) was based on the BET theory (Bansal and Goyal, 2005) and was calculated using the N_2 adsorbed volume at relative pressures of 0.05-0.1. Liquid N_2 volume, referring to the N_2 adsorbed volume at a relative pressure of 0.995, was determined to be the total pore volume (V_t). The mean pore width (W_{mean}) was calculated to be $2V_t/S_{BET}$, in which pores were assumed to be slits. Activated carbons consist of graphite-like sheets between which small slit-shaped pores exist (EI-Sayed and Bandosz, 2002). In the present study, according to Sing et al. (1985), micropores were distinguished into ultramicropores (width less than 0.7 nm) and supermicropores (width from 0.7 to 2.0 nm). The pore size distribution was evaluated using density functional theory (Olivier, 1998 and Ryu et al., 1999). The DFT software developed by Quantachrome Instruments Inc. (version 1.62) was used to obtain the pore size distribution, in which a slit pore equilibrium model was employed. The volumes of ultramicropores (V_u), supermicropores (V_s), and mesopores (V_m) were obtained using the pore size distribution data obtained by the above DFT method.

Adsorptive DBTs Removal Test

Commercial kerosene produced in Japan Energy Corporation, which was Grade-1 quality regulated in Japan Industrial Standard (JIS-K2203), was employed for the adsorptive desulfurization test. The sample was dried at 130 °C in atmospheric air for 3 h prior to the kerosene immersion. The sample of 0.5 g was immersed in the above kerosene of 15.0 g in a 30 mL glass vessel at 10°C for 100 h. Kerosene was not stirred during the immersion, but shaken a few time everyday by hand. The adsorption time of 100 h was confirmed to be sufficient to reach the adsorption equilibrium. The total sulfur content in kerosene was evaluated using a sulfur analyzer based on ultraviolet fluorescence method (9000LLS; Antek Instruments, Inc., USA). The sulfurs embedded in DBTs were identified and quantified using a gas chromatograph-inductively coupled plasma mass spectrometer (GC-ICP-MS, GC 6890N; ICP-MS 7500CS; Agilent Technologies Inc., USA). DBTs are defined as sulfur compounds which contain double aromatic rings and of which molecular mass is larger than that of DBT (molecular mass: 184) in the GC-ICP-MS system. The total sulfur content in the untreated kerosene was evaluated to be 14.1 mass ppm, while the content of sulfur in DBTs therein was 3.5 mass ppm. DBTs adsorption capacity (C_{DBTs}) was represented by the mass of sulfur in adsorbed DBTs divided by the mass of the adsorbent (RHAC sample).

Result and Discussion

Compositional, Textural, DBTs Adsorption Characteristics of Different Types of RHACs

Five types of rice husks activated at the temperature of 850°C for 1 h were provided to compositional analysis. The mass yield of the carbonization and activation process and the elemental composition of the above RHACs are shown in **Table 2**. The level of mass yield is found to be related to the type of rice husk. The RHAC with the lower mass yield is composed of the higher-level carbon and the lower-level ash. High-content carbon and low-content ash are particularly observed on the activated AK-NI and KO-TO.

Table 2. Mass yield and elemental composition of different types of rice husks activated at 850°C for 1 h.

Sample ID	Mass yield (mass%)	H (mass%)	C (mass%)	N (mass%)	S (mass%)	Ash (mass%)	O* (mass%)
AK-OH	33.2	0.4	35.0	0.5	0	61.5	2.6
AK-NI	26.1	0.5	47.3	0.7	0	47.7	3.8
AK-OG	30.6	0.5	40.5	0.8	0	55.1	3.1
HI-HO	34.2	0.6	35.5	0.5	0	60.7	2.7
KO-TO	26.8	0.5	43.6	0.6	0	52.2	3.1

*: by difference and not in ash

Figure 2 shows nitrogen adsorption isotherms on the different types of the rice husks activated at 850°C for 1 h. All the isotherms display a gradual increase in the slope at the relative pressure higher than 0.1 and a hysteresis loop at a high relative pressure, belonging to type IV. A hysteresis loop at a high relative pressure shows an existence of mesopores. The type of rice husk has an influence on the isotherm at only low relative pressure (< 0.1) at the activation conditions of 850°C and 1 h. **Table 3** shows S_{BET} , V_t , and W_{mean} of the different types of rice husks activated at 850°C for 1 h. Large S_{BET} and V_t were observed on the activated KO-TO and AK-NI, with high-content carbon and low-content ash, while the activated AK-OH and HI-HO with low-content carbon and high-content ash provide small S_{BET} and V_t . Large S_{BET} and V_t are found to be responsible for a reduction of the pore width.

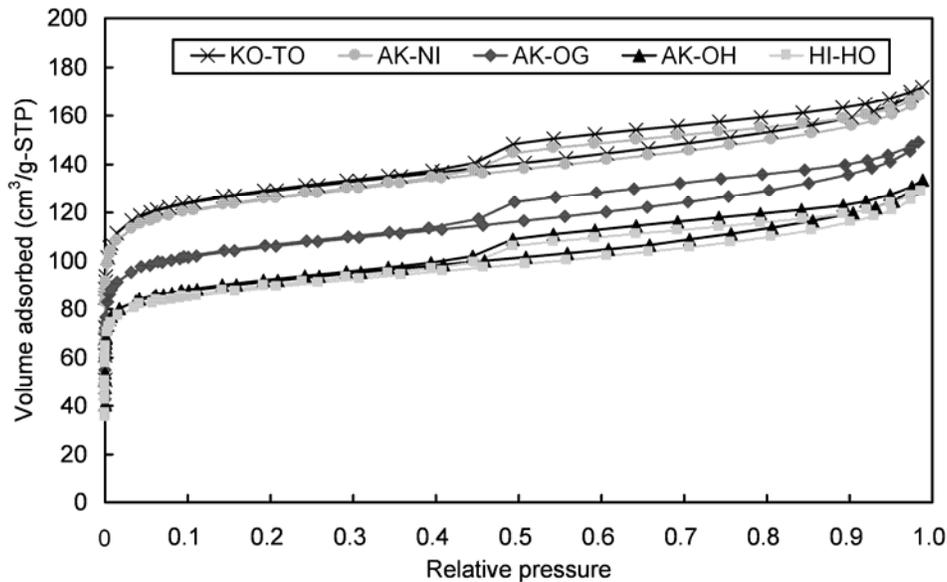


Figure 2. Nitrogen adsorption isotherms at -196°C on different types of rice husks activated at 850°C for 1 h.

Table 3. BET specific surface area (S_{BET}), total pore volume (V_t), and mean pore width (W_{mean}) of different types of rice husks activated at 850°C for 1 h.

Sample ID	S_{BET} (m ² /g)	V_t (cm ³ /g)	W_{mean} (nm)
AK-OH	334	0.207	1.24
AK-NI	460	0.261	1.13
AK-OG	388	0.231	1.19
HI-HO	325	0.200	1.23
KO-TO	473	0.267	1.13

The DBTs adsorption capacities of different types of RHACs were evaluated with a relation to the volume of pores at the similar activation conditions (see **Figure 3**). High values of C_{DBTs} were observed on the activated KO-TO and AK-NI (0.069 and 0.066 mg-S/g-Ads, respectively), which are accompanied by the large V_u and V_s . All the RHACs show a similar level of V_m (0.065-0.070 cm³/g), indicating that the volume of mesopores was not determined by the contents of carbon and ash, but by the activation conditions. Comparable volumes of mesopores were observed on all the RHACs, demonstrating that increases in V_u and V_s enlarge the DBTs adsorption capacity.

The textural and DBTs adsorption characteristics of micro-porous ACF were also evaluated. The textural characteristics and the DBTs adsorption capacities of the ACF and the KO-TO activated at 850°C for 1 h, with the largest adsorption capacity in the RHAC samples, are compared in **Table 4**. Remarkably larger V_s of the ACF (0.614 cm³/g) should contribute to larger S_{BET} and V_t which are respectively 5 and 4-fold greater than those of the activated KO-TO. V_u and V_m of the ACF are about twice larger than those of the activated KO-TO. However, C_{DBTs} of the ACF was 0.090 mg-S/g-Ads, while that of the activated KO-TO was 0.069 mg-S/g-Ads (77 % performance to the ACF). If all the sulfur in DBTs was removed from the used kerosene, the DBTs adsorption capacity should be 0.105 mg-S/g-Ads. The above DBTs adsorption results imply that larger V_s which provides larger S_{BET} and V_t is not so useful for the DBTs adsorption. The roles of V_u and V_m on the DBTs adsorption seem to be important.

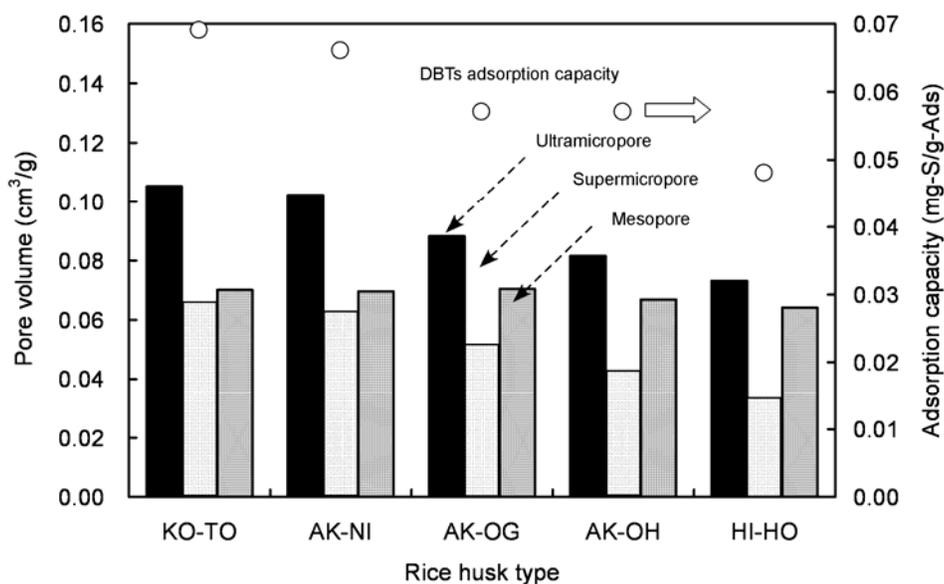


Figure 3. The relationship between DBTs adsorption capacity in commercial kerosene and the pore volumes of ultramicropore, supermicropore, and mesopore on different types of the activated rice husks.

Table 4. A comparison of textural characteristics and DBTs adsorption capacity for activated carbon fiber (ACF) and KO-TO activated at 850°C for 1 h, with the largest adsorption capacity in RHAC samples.

	ACF	Activated KO-TO
S_{BET} (m ² /g)	2336	473
V_t (cm ³ /g)	1.052	0.267
W_{mean} (nm)	0.901	1.128
V_u (cm ³ /g)	0.201	0.105
V_s (cm ³ /g)	0.614	0.065
V_m (cm ³ /g)	0.128	0.070
C_{DBTs} (mg-S/g-Ads)	0.090	0.069

Ania and Bandosz (2006) evaluated the performance of various activated carbons from different carbon precursors as a DBT adsorbent in hexane liquid at 178-S mass ppm. It was shown that the volume of micropores of which width was < 0.7 nm (defined as ultramicropores in this study) governed the amount of the adsorbed DBT, and the adsorption capacity had a linear relation with the volume of those pores. It was also mentioned that mesopores controlled the kinetics of the DBT adsorption process. The size of the DBT molecule is reported to be 0.65 nm (Ania and Bandosz, 2006). DBTs having a plane structure can enter slit-shaped ultramicropores in parallel to the wall surface, which produces a high potential for the DBTs adsorption. Meille et al. (1999) studied the mechanism of DBTs adsorption on a catalyst, suggesting a significance of π electrons in the aromatic rings participating in the adsorption mechanism of DBTs. The interaction of π electrons on graphite-like sheets constituting slit-shaped pores in activated carbons between π electrons in DBTs is likely to further promote an entrance of DBTs in parallel to the wall surface of slit-shaped ultramicropores. Therefore, predominant adsorption sites of DBTs in the RHACs are deemed to be ultramicropores.

An activated carbon of 0.5 g was immersed at 25°C in a model fuel of 10.5 g, in which benzothiophene, DBT, 4-methyl DBT, and 4, 6-dimethyl DBT (each about 100 S-mass ppm) were added (Zhou et al., 2006). The largest adsorption capacity was 7.0 mg-S/g-Ads, which is about 100-fold higher than that of the RHAC greatest in this study. The differences between the present study and the above preceding researches are the sulfur content in the solute. The sulfur content in the preceding works is much higher than that of the kerosene used. At the high sulfur content, it is likely that ultramicropores volume dominates the capacity of DBTs adsorption and mesopores volume has influence on the kinetics of DBTs adsorption. However, at the low sulfur content as in the present study, the DBTs adsorption sites in ultramicropores might not be fully filled. Hence, not only ultramicropores but also mesopores, of which important role is leading DBTs to the adsorption sites, determined the DBTs adsorption capacity. Very large V_s (0.614 cm³/g) of the ACF, resulting in very large S_{BET} and V_t , was not useful for increasing C_{DBTs} . Even though S_{BET} and V_t of the RHACs are not so large, the RHACs have more suitable pore structure which can efficiently adsorb DBTs in the kerosene.

Conclusions

Japanese rice husks were at first carbonated in N₂ and then activated in CO₂ at 850°C for 1 h. The textural and chemical characteristics of the obtained RHACs as well as the ACF having much larger S_{BET} and V_t were evaluated in order to correlate their DBTs adsorption capacity in the kerosene. A feature of the RHACs was very high-content ash making up about half of their mass. The largest C_{DBTs} (77 % performance to the ACF) appeared on the RHAC, with the high-content carbon and the low-content ash in all the RHAC samples. Not only ultramicropores working as the DBTs adsorption sites but also mesopores leading DBTs into the ultramicropores were suggested to determine the DBTs adsorption capacity. A contribution of supermicropores on the DBTs adsorption was minor. Supermicropores, which were much produced in the ACF and provided its large S_{BET} and V_t , were not be beneficial as long as the DBTs removal in the kerosene. Therefore, the RHACs displayed a decent performance when compared to the ACF despite much smaller S_{BET} and V_t , indicating that RHACs produced a textural property suitable to an efficient removal of DBTs in the kerosene.

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